

TRANSIENT KINETIC STUDIES OF CHAR GASIFICATION IN CARBON DIOXIDE

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INTRODUCTION

The rate (R) of a heterogeneous gas/solid reaction (e.g., char gasification) at a given level of solid conversion (X_s) and at constant reactant gas pressure can be expressed in the following form [1,2]:

$$R \equiv \frac{1}{1-X_s} \frac{dX_s}{dt} = kC_s \quad (1)$$

In Equation 1, C_s is the "concentration" of the solid. It is conventionally identified with the total surface area (TSA) of the solid. Two parameters are of primary practical and fundamental interest here: the rate constant (k) and the time (t) necessary to achieve complete solid (char) conversion.

The rate constant for char (carbon) gasification expressed per unit TSA is very much dependent on the origin and/or thermal history of the char [1,3,4]. The rate constant expressed per unit ASA was found to be a function of temperature only, within a factor of 2-3 [1,3].

At constant reactant gas pressure, the complete char consumption time is determined from the following expression:

$$t = \frac{1}{k} \int_0^1 \frac{dX_c}{C_c(1-X_c)} \quad (2)$$

It is seen that the integration of this expression requires the knowledge of the conversion dependence of the char concentration term, i.e., $C_c = f(X_c)$. Laine et al. [5] were successful in determining this functional relationship for the gasification of a graphitized carbon black with oxygen; they determined the unoccupied active surface area (UASA) by taking into account the inhibiting effect of the stable complex formed during the low-pressure reaction. Attempts to determine UASA using the same [6] or analogous [7] approach for less ordered carbons such as coal chars have not been successful, however. A satisfactory correlation was not found between the total active surface area (ASA), measured by low-temperature oxygen chemisorption, and rate variations with conversion [6,7]. The consequences of this finding can best be analyzed by noting that the rate is proportional to the number of reactive sites, i.e., sites at which the carbon-oxygen intermediate forms (at reaction temperature) and decomposes to form gaseous reaction products. These should be distinguished from the sites that give origin to a "stable" complex which inhibits, at least temporarily, the formation of the reaction intermediate [5]. Therefore, Equation 1 can be rewritten as:

$$R = k (TSA) \left(\frac{ASA}{TSA} \right) \left(\frac{RSA}{ASA} \right) \quad (1a)$$

Very few, if any, studies of carbon and char gasification kinetics have attempted the direct determination of the reactive surface area (RSA). In practically all existing kinetic models, for example, the assumption is made that RSA/TSA is constant and the gasification reactivity profiles (reactivity variations with conversion) are thus interpreted on the basis of TSA variations with conversion. More often than not, however, this assumption is not valid [2]. In our experience, the useful simplifying assumption that RSA/ASA is constant is most often valid to within a factor of 2-3 [1,8]. When a more precise comparison of reactivities of different chars is needed or when Equation 2 needs to be solved for a given char, this assumption needs to be relaxed and tested.

The technique of transient kinetics has often been used in heterogeneous catalysis [9]. It has the virtue of being able to provide separately the rate constant and the (re)active site density (RSA). Only recently has its use been suggested [10] and reported [11,12] for providing new insights into carbon (char) gasification kinetics. In this paper, we discuss its application to char gasification in carbon dioxide.

EXPERIMENTAL

Three chars were used in this study: a relatively pure Saran char, prepared from the corresponding copolymer [1]; a bituminous coal char, with a significant quantity of noncatalytic inorganic constituents, obtained from a high volatile A bituminous coal (PSOC 1098) [13]; and a lignite char, with the catalytically active calcium (Dem+Ca) loaded by ion exchange onto the demineralized lignite (PSOC 246) [3,13]. More detailed char characterization is given elsewhere [14].

Figure 1 gives the schematic representation of the experimental system. A char sample (20-70 mg, $<75\ \mu\text{m}$) is reacted in a differential fixed-bed flow reactor (1 cm, ID) and the products are continuously monitored by nondispersive infrared analysis (Beckman, model 864). All samples were heated to 1173 K under flowing N_2 (99.999% purity), and then cooled to the gasification temperature (in the range 950-1130 K, chosen to obtain comparable char reactivities). After partial gasification, the flow of CO_2 (200 cm^3/min , STP) was interrupted and switched back to that of N_2 (200 cm^3/min , STP) at the same reaction temperature. The steady-state and transient response of CO concentration vs. time were monitored by the infrared analyzer.

Preliminary runs were carried out to determine the reaction conditions of temperature, sample size, particle size, and gas flow rate to eliminate mass transfer limitations [14].

RESULTS AND DISCUSSION

Figure 2 shows the steady-state rate variation with conversion (or time) for the bituminous coal char gasified in 1 atm CO_2 at different temperatures. A monotonically increasing specific gasification rate (in g char reacted per hour per unit mass of unreacted char) is observed in all cases. Figure 3 shows the Arrhenius plot for the same char. The activation energy was found to be 60 ± 2 kcal/mol and constant over the entire conversion range; this indicated the absence of transport limitations.

Figure 4 shows typical transient responses observed when the flow or reactant gas (CO_2) was replaced, at a particular conversion level, by that of the inert gas (N_2). The time scale for the achievement of baseline concentration levels of the product (CO) was of the order of minutes for all samples. With no sample in the reactor (blank experiment), this time scale was of the order a few seconds.

The well known and generally accepted [15] mechanism of the reaction, involving free carbon (re)active sites (C_f), was assumed:



The reaction rate is equal to the rate of decomposition of the C-O intermediate. The integrated area under the transient response curve, such as shown in Figure 4, gives the concentration of C-O intermediates (i.e., RSA) at the conversion level at which the steady-state reaction was interrupted.

Figures 5-7 show the results of transient kinetic experiments for the three chars used in this study. In all cases both the reaction rate and RSA monotonically increase with conversion. The reactive surface area of the lignite char, in which CaO acts as an efficient CO_2 dissociation center (catalyst) [3], is seen to be almost an order of magnitude higher than the RSA of the Saran and bituminous coal chars, in which CO_2 dissociation occurs predominantly on the carbon (re)active sites. It is interesting to note that RSA of the latter two is one order of magnitude smaller than their ASA (low-temperature oxygen chemisorption capacity) [1]. It is two orders of magnitude higher, though, than the relatively low value obtained by Freund [11] for a Carbosieve, also a highly disordered carbon, gasified in CO_2 at 850-980 K.

In complementary studies [7,16], we have found that the amount of stable complex (remaining on the char surface after partial gasification and subsequently removed at higher temperatures by temperature-programmed desorption) on these chars also increases monotonically with conversion, by a factor of about 3-4. The oxygen chemisorption capacity (ASA) of the bituminous coal char, on the other hand, exhibited a maximum value at an intermediate conversion level, therefore indicating that RSA/ASA varies with conversion. Two practical consequences of these findings have emerged [1,16]:

- (1) For a quantitative explanation of char reactivity profiles, direct measurements of RSA are necessary; the amount of stable complex on the char surface can also be used, at least qualitatively, because it seems to correlate well with RSA.
- (2) For a quantitative explanation of reactivity differences among different chars, ASA is good to within a factor of 2-3; the amount of stable complex on the chars surface cannot be used because it is very sensitive to the reaction temperature and its value decreases with increasing temperature.

From a fundamental standpoint, two issues need further discussion: (1) the reason for the apparent existence of a qualitative correlation between RSA and the amount of stable complex on the surface of a char at a given temperature; (2) the existence of a turnover frequency for char gasification. The former is discussed in some detail elsewhere [16,17]; suffice it to say here that "stable" complex formation should be regarded not only as a temporarily inhibiting process [5], but also as an intermediate step in the mechanism of gasification, particularly for disordered carbons and at relatively high pressures.

Figure 8 shows excellent linear relationship between reactivity and RSA for the three chars analyzed in this study. Thus obtained rate constants (see Equation 1a), or turnover frequencies [18], are seen to be independent of conversion. Their values are 20.8 h^{-1} (1133 K), 14.4 h^{-1} (1093 K), and 4.0 h^{-1} (953 K) for the Saran char, bituminous coal char and Dem+Ca lignite char, respectively. These are, not unexpectedly, relatively low values compared to the commonly encountered catalyst turnover frequencies of 1 s^{-1} [18]. It is also interesting to compare the turnover frequency for the Dem+Ca lignite char obtained here with that obtained for a similar char gasified with O_2 [19]; the latter value (about 0.3 s^{-1}) is several orders of magnitude higher, as expected. A comparison of turnover frequencies of the Saran char and the bituminous coal char at

the same temperature is also interesting. At 1103 K, these are 9.8 h^{-1} and 16.8 h^{-1} , respectively [14]. This suggestion of possible structure sensitivity [18,20] of char gasification is being investigated further in our laboratory.

SUMMARY AND CONCLUSIONS

The analysis of char gasification in CO_2 using the transient kinetic approach gives a direct measurement of the reactive surface area of chars. The use of this technique has also provided the heretofore elusive quantitative experimental explanation of reactivity variations with conversion. It was found that the ratio of the reactive surface area of a bituminous coal char to its active surface area is not constant, but varies as a function of conversion. Turnover frequencies for char gasification in CO_2 have been determined. Preliminary experiments suggest that char gasification may be a structure-sensitive reaction.

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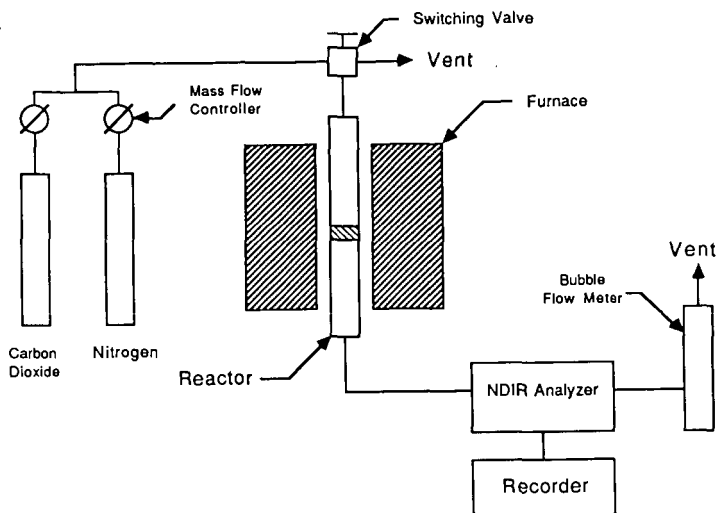


Figure 1. Schematic representation of the experimental system for transient kinetic studies.

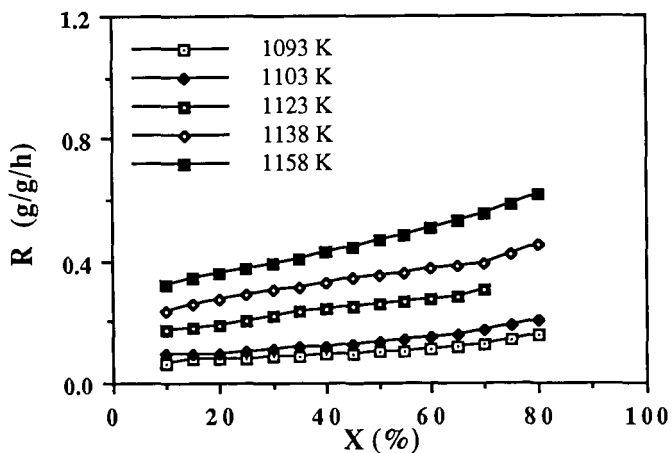


Figure 2. Typical steady-state responses of the experimental system: specific rate vs. conversion for the gasification of bituminous coal char in 1 atm CO_2 .

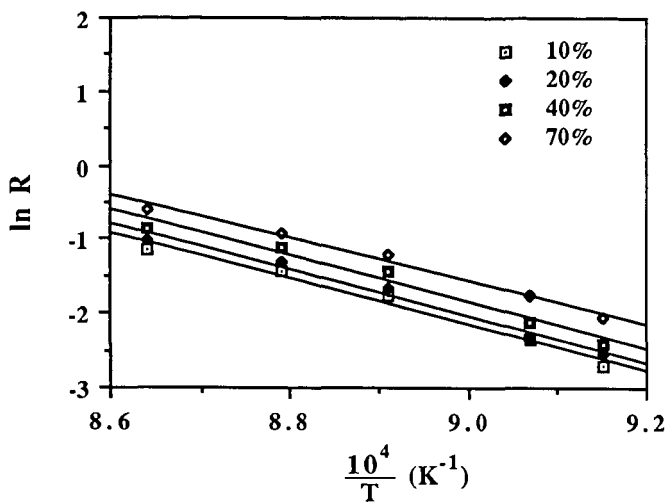


Figure 3. Arrhenius plot for the gasification of bituminous coal char in 1 atm CO_2 .

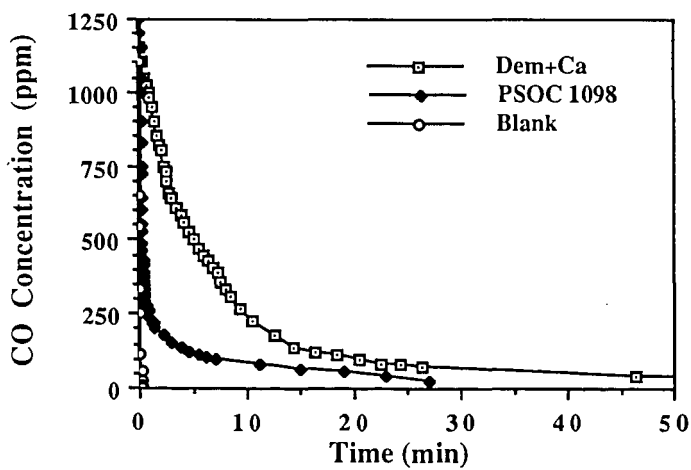


Figure 4. Typical transient responses of the experimental system.

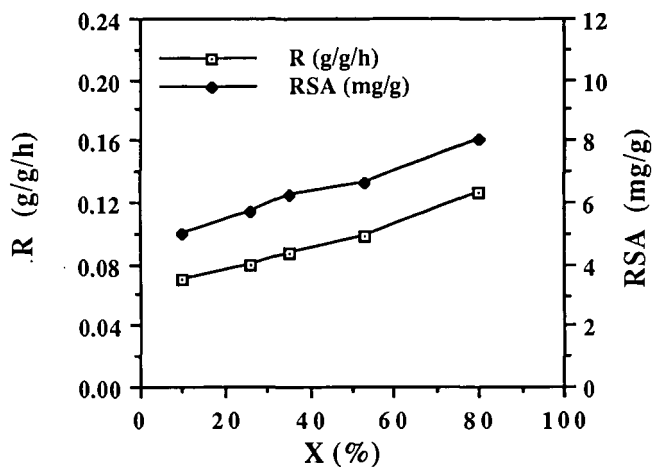


Figure 5. Specific rate and reactive surface area vs. conversion for the bituminous coal char gasified in 1 atm CO₂ at 1093 K.

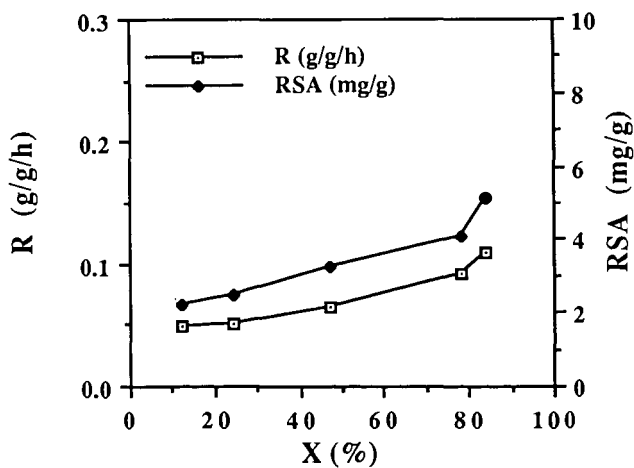


Figure 6. Specific rate and reactive surface area vs. conversion for Saran char gasified in 1 atm CO₂ at 1133 K.

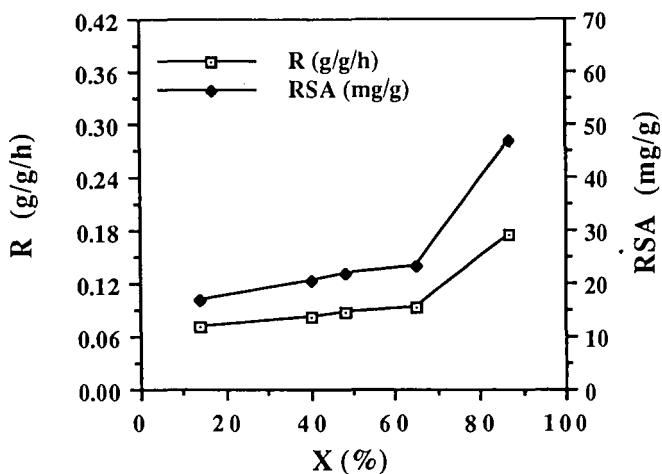


Figure 7. Specific rate and reactive surface area vs. conversion for Dem+Ca char gasified in 1 atm CO₂ at 953 K.

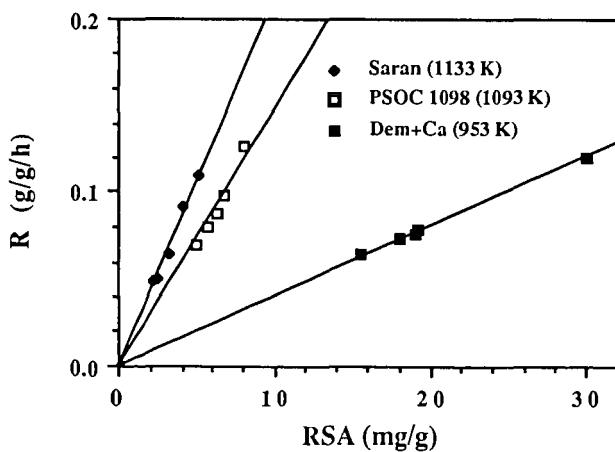


Figure 8. Determination of turnover frequency for the gasification of chars in 1 atm CO₂.